Evaluation of hardened state properties of GGBS-PC mortars modified by superabsorbent polymers (SAP)

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EVALUATION OF HARDENED STATE PROPERTIES OF GGBS-PC MORTARS MODIFIED BY SUPERABSORBENT POLYMERS (SAP)

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Abstract

This paper evaluates the effects of superabsorbent polymers (SAP) on autogenous shrinkage, mechanical properties and microstructural characteristics of mortars with different levels of cement replacement by ground granulated blast-furnace slag (GGBS). Two types of SAPs with different water absorption capacities in cement-paste solution have been considered. The effects of SAP on mortars have been assessed during the first 28 days. The results showed that both polymers used notably reduce autogenous shrinkage. Moreover, the type of SAP has an effect on the pore structure formation in hardened mortars and consequently influences their mechanical properties.

1. INTRODUCTION

Despite their worldwide popularity, cementitious materials are susceptible to cracking, triggered by self-desiccation processes and subsequent autogenous shrinkage. This effect can even be more critical in concrete with ground granulated blast-furnace slag (GGBS), as seen in previous studies [1]-[5].

In an attempt to limit autogenous shrinkage, superabsorbent polymers (SAP) can be used as internal curing agents. Basically, SAP is a cross-linked network of hydrophilic polymers with the ability to absorb and retain large volumes of water [6]-[7]. Figure 1 shows SEM micrographs of a SAP in dry and wet conditions. Due to its high capacity to provide water-filled cavities in hardened state, SAP may facilitate hydration processes and lead to densification of internal structure.

However, their full effect on the microstructure of hardened mortars is still unclear, especially in blended cements [8]-[12], in particular GGBS. Despite a slight retardation of strength development, long-term strength of mortars containing blended cements is not necessarily negatively affected by SAP [10]. In fact, SAP can promote creation of a dense network of

CSH even in a collapsed state and subsequently lead to pores closures [11]. In this case, the effect of SAP is dual and counteracting due to its capacity to increase porosity and improve microstructure [10].

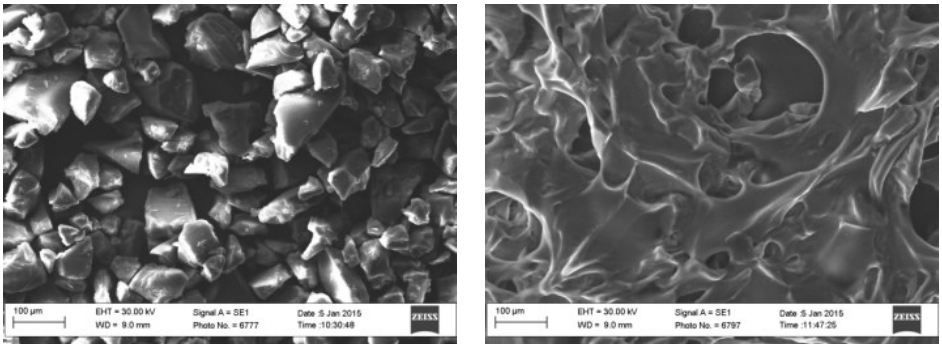

Figure 1: SEM micrographs of SAP in dry and wet conditions respectively.

The effects of SAP on mechanical properties and porosity strongly depend on the polymer type and its water absorption/desorption kinetics [7][11][13]. Although [10] and [12] have considered the use of GGBS in their studies with SAPs, there is still no consensus on the combined effect of slag and polymers on hardened state mortars. Therefore, the paper aims to evaluate this effect by analysing mortars with different levels of cement replacement by GGBS. The investigation has endeavoured to relate the microstructural features with mechanical properties of mortars with GGBS-PC cements during the first 28 days.

2. MATERIALS AND METHODS

Mortars with different mix proportions were produced for the experimental study, considering different levels of Portland Cement (PC) replacement (CEM I 52.5N) by GGBS and different types of SAPs, including reference mortars without GGBS and/or SAP.
Four levels of PC replacement by GGBS: 0%, 25%, 50% and 75% of the binder content (by mass) have been analysed. Table 1 shows the chemical and physical analyses of binder (CEM I and GGBS) used in the experimental study.

Table 1: Chemical and physical analyses of CEM I and GGBS.

	Compound (%)										Fineness (m^2/kg)
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**K_2O**	**Cl**	**LOI**	
CEM I	20.07	4.85	2.72	62.44	2.20	3.15	0.31	0.62	0.06	2.77	410
GGBS	34.53	13.14	0.21	38.53	9.74	0.35	0.17	0.59	0.02	0.64	390

Two different types of SAP have been used in the proportion of 0.25% by mass of binder: SAP X and SAP Y with water absorption capacities of 25-30 g/g and 35 g/g respectively, in cement paste solution. Both SAPs have particles sizes in the range of 63-125 µm.
Fine sand contained 99.95% of particles below 0.6 mm [14]. Table 2 shows the mix proportions of all materials used for mortars preparation.

Table 2: Mix proportions of materials used for mortars production.

Sample name	Type of SAP	CEM I (%) [a]	GGBS (%) [a]	SAP (%) [b]	Binder / Sand (b/s)	Water / Binder (w/b)
R0	-	100	-	-	1:2	0.50
R25	-	75	25	-	1:2	0.50
R50	-	50	50	-	1:2	0.50
R75	-	25	75	-	1:2	0.50
X0	SAP X	100	-	0.25	1:2	0.50
X25	SAP X	75	25	0.25	1:2	0.50
X50	SAP X	50	50	0.25	1:2	0.50
X75	SAP X	25	75	0.25	1:2	0.50
Y0	SAP Y	100	-	0.25	1:2	0.50
Y25	SAP Y	75	25	0.25	1:2	0.50
Y50	SAP Y	50	50	0.25	1:2	0.50
Y75	SAP Y	25	75	0.25	1:2	0.50

[a] of the binder content
[b] by mass of binder

Autogenous shrinkage (AS) was tested by the corrugated tubes method [15] (min 3 specimens for each mortar) from the final setting time until the age of 28 days, using a digital bench dilatometer. Mechanical properties were evaluated by standard flexural (3 samples for each mortar) and compressive (6 samples for each mortar) strengths determination methods [16] at ages of 7, 14 and 28 days. Specimens were cast into prismatic moulds (160 x 40 x 40 mm) and cured in the climate chamber (T = 21 ± 2 ºC and RH = 40 ± 5%). Microstructural features were tested in terms of total porosity (%), median pore diameter (by volume), bulk density at 52 psia (g/ml) and pore size distribution (nm), using Mercury Intrusion Porosimetry (MIP) technique.

3. RESULTS AND DISCUSSION

Figure 2 shows the results of autogenous shrinkage (AS) over 28 days. Overall, SAP reduced AS of mortars with and without GGBS compared with the reference samples.

Considering samples without SAP, autogenous shrinkage steadily increased considering different GGBS contents over the time. The higher level of cement replacement by GGBS, the greater was AS. At the end of 28 days, shrinkage values of about 350, 480, 560 and 640 µm/m for mortars with 0%, 25%, 50% and 75% of GGBS respectively were observed.

Some authors attribute this increment in AS to a higher degree of hydration of GGBS, and therefore, greater degree of self-desiccation [2]-[4]. As a result of slag hydration, the amount of water in pores is reduced, leading to self-desiccation. In addition, CSH formed during the reaction produce a chemical shrinkage, since the volume of the hydrated products is less than the sum of volume of water plus initial anhydrous products [5]. Thus, greater chemical shrinkage can lead to a faster and more intense self-desiccation, and results in larger AS. However in some cases, as in the current study, GGBS may slow down the hydration rate due to its larger particles when compared to PC (Table 1) and most importantly due to the lower amount of PC (lower alkali content required for activation of slag hydration). In this case, the use of GGBS may lead to finer pores, which in turn results in increased AS. The smaller capillaries the higher is tensile stress provoked by water menisci between the pores walls [5]. In any case, the increment of GGBS content can lead to formation of material which is more prone to deformation.

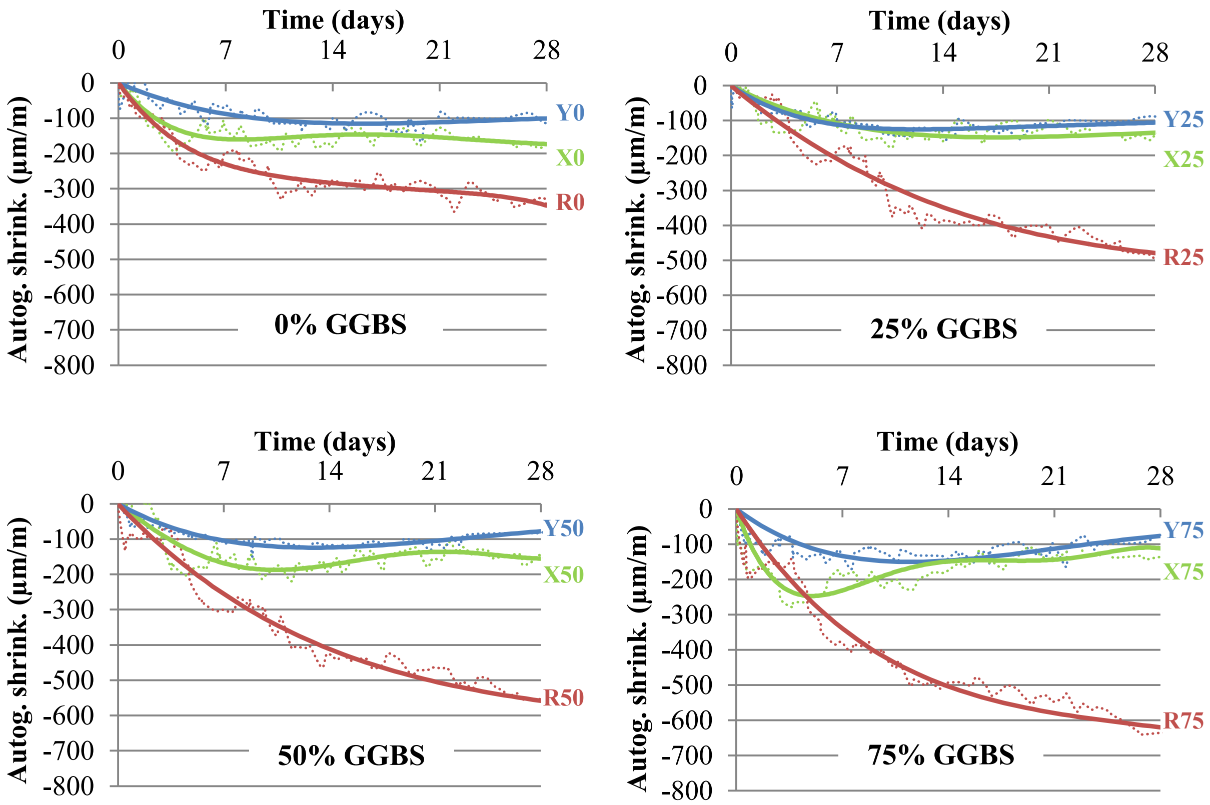

Figure 2: Results of autogenous shrinkage.

However, in the presence of SAP, this behaviour was sharply altered showing a significant reduction in AS for all levels of cement replacement by GGBS. Autogenous shrinkage was mitigated when using internal curing by SAP in mortars with slag. This reduction was also verified in cement paste with GGBS modified by SAP [12]. The principle of internal curing by means of SAP relates to the provision of water-filled cavities in hardened mortars, reducing AS [10]. Regarding the studied samples, SAP Y seemed to have better performance than SAP X, indicating different efficiencies for different polymers. However, all shrinkage values varied between 75 and 175 μm/m at 28 days. They represent reductions between 40 - 80% for SAP X and 65 - 90% for SAP Y, in comparison with reference mortars with the same GGBS content. As the slag content is increased, the reduction in autogenous shrinkage is more pronounced. It suggests that SAP has a positive effect on AS reduction, especially for high contents of slag when this diminution is maximized.

The results of compressive strength are shown in Figure 3. Overall, the increment of GGBS has reduced the compressive strength during the first 28 days.

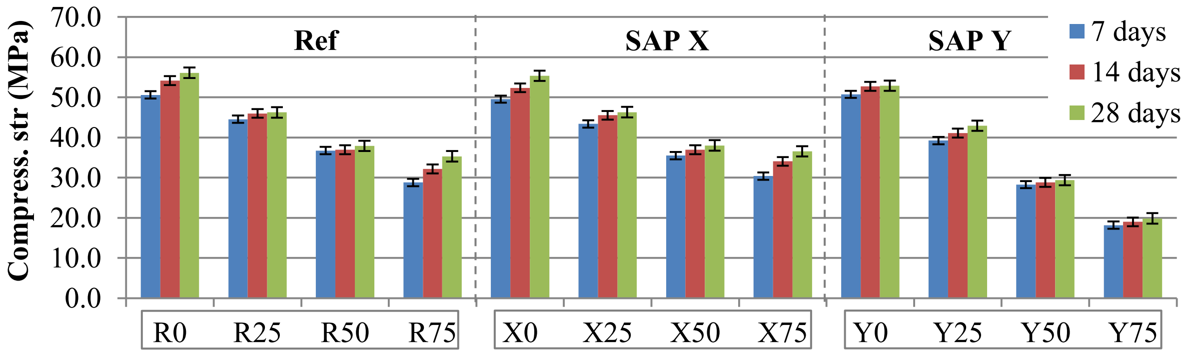

Figure 3: Results of compressive strength.

The reduction of compressive strength for samples with higher contents of GGBS can be related to its slower process of hydration. This is because the higher the amount of GGBS, the lower is the content of calcium hydroxide responsible for the activation of hydration. It is expected that these reactions intensify and hydrated calcium silicates are formed in long term, resulting in mechanical strength similar to the reference mortar [5].

Besides, as it appears, the fineness of slag can also affect the rate of reaction. As seen in Table 1, GGBS particles considered in this study are bigger than those of cement Portland, thereby contributing to slower rates of reaction and hence, lower values for early strengths. As slag is not fine enough when compared with Portland cement, only a small part of it can react in the first weeks and the remainder may act as an inert aggregate, thereby reducing the overall strength.

Moreover, it is evident that the polymer type can have an influence on mechanical properties. SAP X seems to have similar performance to the reference sample for all ages tested. It indicates that SAP X can keep the same level of compressive strength when compared to all reference samples regardless of the GGBS contents. However, mortars with SAP Y seems to have lower compressive strength as the GGBS content is increased when compared with the respective sample without SAP. The reduction of strength at 28 days is in the order of 6%, 7%, 23% and 44% in comparison with the reference sample with 0%, 25%, 50% and 75% of slag content respectively. Thus, the type of SAP can affect compressive strength of mortars.

The results of flexural strength testing are shown in Figure 4. In general, increase of level of PC replacement by GGBS can lead to lower flexural strength during the first 28 days.

Flexural strength had the same pattern of compressive strength when the addition of GGBS is considered. The greater the GGBS content, the lower was the strength during the first 28 days. The GGBS may have led to a lower rate of reaction resulting in lower values of mechanical properties in early ages.

Mortars with SAPs seem to have similar flexural strengths than the reference sample in the first days. However, with the exception of the mortar with high content of GGBS, samples with SAP X seem to have lower flexural strengths at 28 days. This reduction was less than 10% of the respective reference sample. While SAP X has slightly reduced flexural strength, SAP Y has increased those values in comparison with the reference samples.

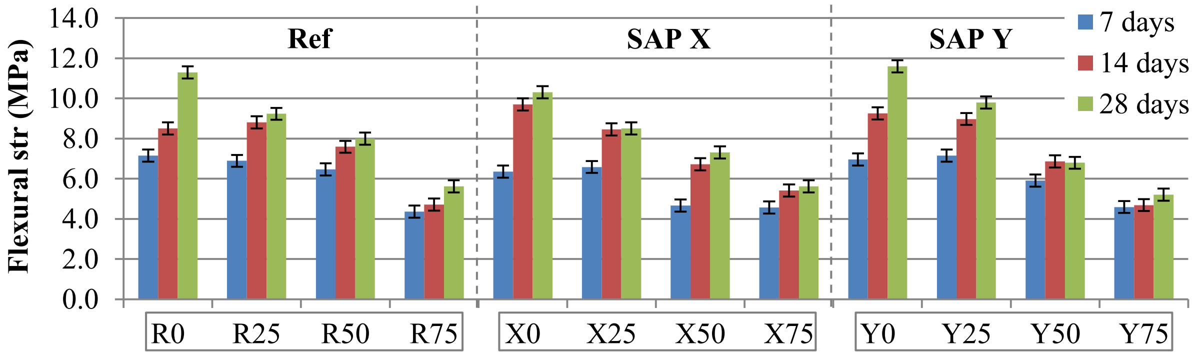

Figure 4: Results of flexural strength.

This shows how the type of SAP, regarding its sorption capacity and kinetics, can influence mechanical properties of cementitious materials. Usually, premature release of water by SAP (before setting) into the cement-based matrix may lead to some decrease in mechanical strength. This effect can be attributed to some increase in the effective water/cement ratio and subsequently to higher porosity of mortar [13][17].

In contrast, for mixes with SAP that do not exhibit early water desorption, either no decrease or only a very moderate decrease in strength can take place. This may be explained by the release of stored water at later stages. In this case extra water may serve truly as internal curing water. The efficient mitigation of autogenous shrinkage and the enhanced degree of hydration seem to be sufficient to balance the negative effect of voids induced by SAP particles, since they have low desorption ratio [13].

In order to better understand the effect of SAP pores on the mechanical properties, microstructural characteristics of studied mortars were also analysed. The results of total porosity, median pore diameter (by volume) and bulk density obtained by means of MIP technique are shown in Table 3. Addition of SAP and higher contents of GGBS led to increased overall porosity during the analysed period. However, the type of SAP could define size of pores over time and influence mechanical features.

Overall, bulk density varied between 1.88 – 2.04 g/mL for all samples in every age analysed. This range decreased at 28 days when the samples showed some variations between 1.93 – 2.01 g/mL. As bulk density is inversely proportional to porosity, the greater the porosity, the lower is the bulk density. In this way, bulk density seems to decrease with SAP addition as well as with the increment of GGBS content.

The addition of GGBS seems to lead to increased porosity and increased median pore diameter. The higher the level of PC replacement by GGBS, the greater is the porosity and the pore size diameter during the first 28 days. It can be related to a low rate of slag reaction in comparison with higher contents of PC in the early ages. This increment in porosity may be directly associated with lower mechanical strengths as presented in Figures 3 and 4. Moreover, some authors [5] have related such increment of porosity by GGBS to the increase in autogenous shrinkage, as seen in Figure 2. The higher is the quantity of GGBS the higher the total pore volume, and hence the higher the likelihood of deformation. GGBS can also provide greater amount of finer pores (below 20 nm), as seen in the pore size distribution curves (Figure 5). The higher the GGBS content, the more significant is the presence of smaller pores in the cementitious matrix. The finer structure of pores can lead to a greater shrinkage generated by the water menisci in the capillaries as discussed above.

Table 3: Microstructural features by MIP technique.

Sample name	7 days			14 days			28 days		
	Porosity (%)	**Median pore diameter (nm)**	**Bulk density (g/mL)**	**Porosity (%)**	**Median pore diameter (nm)**	**Bulk density (g/mL)**	**Porosity (%)**	**Median pore diameter (nm)**	**Bulk density (g/mL)**
R0	16.4	53.9	2.00	16.8	80.0	2.03	16.8	99.3	2.01
R25	18.1	82.9	2.04	19.5	140.3	2.00	19.7	234.2	1.97
R50	21.8	194.9	1.96	20.0	174.9	1.99	17.6	252.3	2.00
R75	21.8	196.6	1.97	21.2	236.4	1.98	18.9	496.6	1.95
X0	20.1	75.6	2.01	19.9	78.3	1.98	17.6	94.2	1.97
X25	19.8	98.0	1.96	20.8	140.0	1.97	19.0	180.6	1.95
X50	22.7	178.8	1.90	21.7	214.9	1.92	21.6	254.2	1.90
X75	22.3	53.7	1.94	21.9	70.7	1.91	20.3	49.6	1.93
Y0	19.0	58.9	2.01	14.0	55.9	2.01	17.9	114.9	1.97
Y25	22.8	296.7	1.89	20.6	380.3	1.89	17.3	193.8	1.96
Y50	25.8	502.4	1.90	21.6	426.4	1.94	23.3	551.8	1.93
Y75	25.1	724.8	1.92	23.7	813.3	1.88	21.7	715.6	1.93

SAP can also have a significant effect on the porosity of mortars. Depending on its sorption capacity and kinetics of the process, different sizes of pores can be left behind as SAP dries out in the cement matrix [11]. According to Table 3, SAPs facilitate increase in total porosity of mortars but also induce formation of different median pore diameters which in turn may influence compressive and/or flexural strength.

For instance, mortar with SAP X seemed to have smaller pores than the reference sample at 28 days. This trend may be observed in Figure 5 by comparing the reference and SAP X curves. As GGBS content is increased, the peaks formed by SAP X tend to shift to the right when compared with those formed by the reference samples, indicating a reduction in pores size diameter. In fact, this can also be observed when median pore diameters are compared for the same age of 28 days (Table 3). Despite higher porosity, SAP X seemed to produce smaller pores which may be more significant for flexural strength analysis. Samples with SAP X indeed presented lower values of this property than those obtained for reference mortars with the same slag content (Figure 4). Thus, SAP X can lead to decrease of pore size at 28 days, especially for higher quantity of GGBS, resulting in lower flexural strength. This reduction in pore size can be associated with the formation of hydration products that fill SAP voids facilitating formation of denser and more homogenous cementitious matrix [11]. Although

SAP X increases the total volume of pores, it can lead to formation of finer pores during the first 28 days.

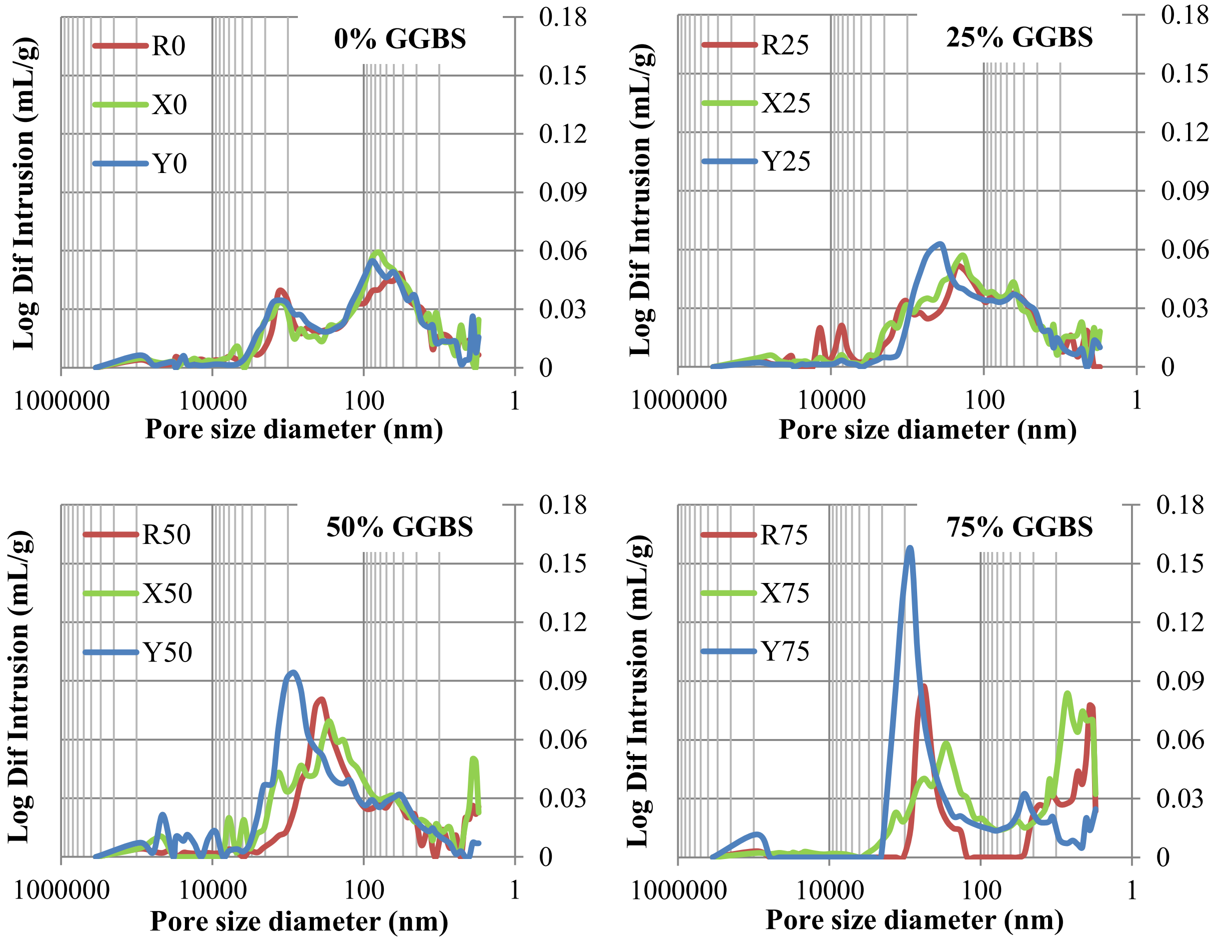

Figure 5: Pore size distribution curves at 28 days.

Nevertheless, SAP Y seems to produce bigger pores when compared to samples without polymer. This increment in total porosity and pore size diameter can be verified by comparing both samples in Table 3 and Figure 5. In general, median pore diameter was larger for SAP Y samples when compared with the corresponding reference sample (same GGBS content) (Table 3). Also, the peaks of pore size distribution curve for SAP Y seemed to be shifted left, relative to the reference curve, representing increase in pore diameter (Figure 5). This difference is more pronounced for higher slag contents. This enlargement of pores can mainly affect compressive strength; these values were lower than those for reference samples with higher quantity of slag (Figure 3). While releasing internal curing water, SAP shrinks and leaves behind air voids, which act as weak spots in the material structure [7]. The formation of larger pores by SAP Y may be related to its higher water absorption capacity compared with SAP X. The higher the water absorption, the higher is the capacity to swell and form larger water reservoirs. When this water is released, bigger pores may be produced. Thus, although [18] have suggested that the differences in sizes and quantities of SAP pores do not have an effect on strength development, the results showed that the pores formed by collapsed SAPs can affect mechanical strength in mortars with GGBS-PC cements up to 28 days. However, shape of mercury intrusion-extrusion hysteresis (Figure 6) indicates the pores are not well interconnected [11]. It is likely that these pores are of "ink-bottle" shape and/or are closed. Because of that, despite an increased porosity, the overall durability of SAP modified mortars is not compromised. In fact, durability can be improved by SAP modification [10].

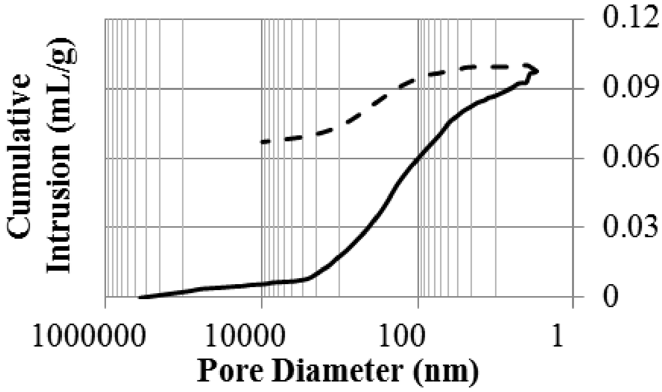

Figure 6: Typical intrusion-extrusion hysteresis.

Therefore, the sorption capacity and kinetics of SAPs can affect the pore structure formation and consequently influence mechanical properties of hardened mortars.

4. CONCLUSIONS

From the results obtained in the experimental study, the following can be concluded:

- Mortars with SAP can significantly decrease autogenous shrinkage (AS) for any studied GGBS content in comparison with the reference mortar. Reduction in AS is maximized for mortars with high quantity of GGBS, where the diminution is over 80%. The reduction of AS by SAP may decrease cracking susceptibility and hence increase sustainability level of cementitious material for more durable constructions;
- Mortar mixes with SAP X tend to have similar compressive strength but lower flexural strength, compared with the reference sample. This is because SAP X facilitates formation of smaller pores during the first 28 days, especially for high content of GGBS. However, SAP Y had a different performance; mortars with this polymer may develop larger pores than reference samples. This effect results in reduction in compressive strength at 28 days, in particular for high quantity of GGBS;
- SAP X seems to be more efficient in clogging their own pores (formed by itself) with products of hydration over the first month. In turn, SAP Y, which presents higher water absorption capacity, is responsible for creating larger pores in the matrix. Overall, although both SAPs increase the total porosity of mortars, these voids can be considered closed and/or "ink-bottle" shape.

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